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Characterization of Niobium-zirconium Mixed Oxide as a Novel Catalyst for Selective Catalytic Reduction of NO_x

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Abstract The performance of mixed niobium-zirconium oxide in the SCR of NO_x with propene in excess oxygen has been studied. The mixed oxide is prepared by impregnation of hydrated zirconia with acidic solution (pH 0.5) of peroxoniobium(V) complex, $[Nb_2(O_2)_3]^{4+}$, ensuring ZrO_2: Nb_2O_5 mole ratio of 6:1. The calcined sample (denoted as 25NbZ-P) has the structure of $Zr_6Nb_2O_{17}$. According to the catalytic test, the conversion of NO_x over the 25NbZ-P catalyst passes through a maximum at 220 °C. Based on the in situ FT-IR results, a reaction mechanism is proposed with nitroacetone and NCO species as the key reaction intermediates. The results of the investigation show that the catalytic properties of the $Zr_6Nb_2O_{17}$ solid solution could be of interest regarding the development of low-temperature catalyst for the SCR of NO_x with hydrocarbons.

Keywords Zirconia-niobia solid solution · C_3H_6-SCR of NO_x · Catalytic activity · In situ FT-IR spectroscopy · Reaction mechanism

1 Introduction

Nitrogen oxides, NO and NO_2 (collectively referred as NO_x) are harmful pollutants exhausted from mobile and stationary combustion engines. In the recent years, the NO_x emissions have been severely restricted especially for automobiles. Diesel and lean-burn gasoline engines are outstanding with respect to fuel efficiency [1, 2]. However, they emit more NO_x when compared to conventional gasoline engines equipped with a three-way catalyst. The exhaust typical for diesel and lean-burn gasoline engines contains an excess of oxygen and this requires a catalytic process that allows for successful reduction of NO_x in competition with the reduction of oxygen. Reduction of NO_x using either the residual hydrocarbons or on-board fuel would be the most ideal technology. However, the traditional materials developed for the selective reduction of NO_x with hydrocarbons (HC-SCR) do not show sufficient activities under the conditions of lean exhaust especially at low temperatures (<150–250 °C) [3–6]. There is still interest in finding a direct HC-SCR catalyst, which possesses high activity in the low-temperature range, good hydrothermal stability and good sulfur tolerance.

Despite of the fact that niobium-containing materials show potential applications in various oxidation and acid-catalyzed reactions [7, 8], a little attention has been given to the performance of these catalysts in the SCR of NO_x. Regarding the reduction of NO with hydrocarbons in excess oxygen, Hinode and co-workers [9, 10] reported that niobium oxide supported on titania is active in the reaction with ethene and propene showing maximum NO conversion of 30 and 62%, respectively, at about 375 °C. Using a mechanical mixture of Nb/TiO_2 and Mn_2O_3 improves the activity in the SCR with propene and lowers the temperature of maximum NO conversion to 200–300 °C [11]. Kikuchi and Kumagai investigated the catalytic performance of Nb-promoted Ag/Al_2O_3 and Co/Al_2O_3 catalysts in the SCR of NO_x in diesel engine exhaust using light gas oil as reductant [11, 12]. The catalytic activity of the promoted catalysts was higher than that of the un-promoted ones and the adsorbed amount of sulfur was lower on the

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Nb-containing catalysts. It has been reported that the deposition of niobium on the surface of alumina lowers the concentration of basic sites [13] which should result in improved resistance to SO_2 poisoning.

Ziolek and co-workers investigated the possibility for application of Pt-promoted niobiosilicate ordered mesoporous materials (NbMCM-41) as NO_x storage (NSR) and C_3H_6-SCR catalysts [14–16]. The presence of niobium in the MCM-41 matrix enhanced the oxidative properties of the catalyst and NO was adsorbed in the form of nitrite/nitrate species [14, 15]. However, the latter species were bound strongly to the surface which hindered their further interaction with propene. The introduction of zirconium near niobium in the MCM-41 matrix weakened the bond of the nitrites/nitrates with the niobium species and enhanced the SCR selectivity [16]. Based on the results of in situ FT-IR study we proposed recently that the Pd-promoted $Zr_6Nb_2O_{17}$ solid solution has the potential of a catalyst for the selective reduction of NO with methane [17]. The Pd-free mixed oxide is thermally stable [18] and has high permanent Brønsted acidity [17].

The analysis of the literature data reveals that the oxide-based catalysts containing niobium may represent an alternative to the current catalytic materials for HC-SCR of NO_x. The aim of this paper was to test the activity of $Zr_6Nb_2O_{17}$ solid solution in the SCR of NO_x with propene. In order to determine the reaction route, we carried out in situ FTIR investigations of the adsorption and co-adsorption of the reagents followed by their interactions at various temperatures. According to our knowledge, there are no reports dealing with the DeNOx properties as well as with NO interaction with propene in the presence of oxygen on such kind of a material.

2 Experimental

The mixed zirconia-niobia was prepared by impregnation of hydrated zirconia with acidic solution (pH 0.5) of peroxoniobium(V) complex, $[Nb_2(O_2)_3]^{4+}$, ensuring ZrO_2:Nb_2O_5 mole ratio of 6:1. After drying, the material was calcined at 600 °C for 2 h. The BET surface area of the calcined material (denoted as 25NbZ-P) was 42 m^2/g. According to XRD the obtained sample has the structure of $Zr_6Nb_2O_{17}$ [17]. The adsorption of 2,6-dimethylpyridine on the 25NbZ-P sample revealed the presence of strong Brønsted acidity. Details about the method of preparation and characterization of the surface acidity are given elsewhere [17].

The catalytic test of NO_x reduction by propene was carried out in a tubular flow reactor (quartz glass) with an internal diameter of 6.0 mm. The catalyst sample was loaded in the form of particles with irregular shape and size of 0.6–1.2 mm. The gas analysis was performed using on-line analyzers as follows: $NO/NO_2/NO_x$ (Environment S.A., Model 31 M), $CO/CO_2/O_2$ (Maihak), THC (ThermoFID). Gas supply section was based on mass-flow controllers manufactured by Bronkhorst. The catalyst was tested at GHSV of 10,000 h^{-1}. The reaction mixture used contained 245 ppm of NO_x ($NO/NO_2 = 1.77$), 504 ppm C_3H_6, 9 vol. % of oxygen and nitrogen for balance to 100 vol. %. The steady-state test was made upon step-wise increase of the reaction temperature and holding at each temperature ($\sim$1.5 h) to reach a constant conversion value. The conversion degrees of NO_x (taken as a measure of the catalytic activity) and propene were calculated using the inlet and outlet concentrations.

The FT-IR spectra were recorded using a Bomem Hartman & Braun MB-102 model FT-IR spectrometer with a liquid-nitrogen cooled MCT detector at a resolution of 4 cm^{-1} (128 scans). The self-supporting discs ($\sim$0.01 g/cm^2) were activated in the IR cell by heating for 1 h in a vacuum at 450 °C, and in oxygen (100 mbar, passed through a trap cooled in liquid nitrogen) at the same temperature, followed by evacuation for 1 h at 450 °C. The experiments were carried out under static conditions. The spectra of the adsorbed compounds were obtained by subtracting the spectra of the activated samples from the spectra recorded. The sample spectra were also gas-phase corrected. The gases NO (99.9%), and C_3H_6 (99.9) used in the in situ FT-IR experiments were supplied by Air Products.

3 Results

3.1 Catalytic Activity

Figure 1 shows the NO_x reduction activity of 25NbZ-P catalyst at various temperatures. The NO_x conversion (Fig. 1, curve (a)) reaches 62% at 220 °C and than decreases as the combustion of propene becomes predominant (Fig. 1, curve (b)). The conversion of C_3H_6 is close to 100% at 250 °C. The catalyst displays stable activity at the temperature of maximum NO_x conversion (the duration of catalytic activity tests was limited to 10 h). The results show that the catalytic properties of the 25NbZ-P sample could be of interest regarding the development of efficient HC-SCR catalyst that could be active at typical diesel exhaust-gas temperatures ($\leq$300 °C).

3.2 FT-IR Spectroscopic Measurements

3.2.1 Co-adsorption of NO + O_2 on the 25NbZ-P Catalyst

Figure 2a shows the spectrum of the gas phase detected at room temperature immediately after the admission of a gas mixture containing 10 mbar of NO and 20 mbar of O_2 to the

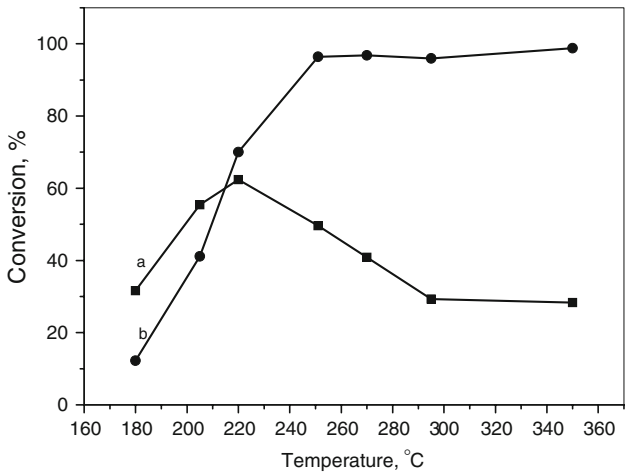


Fig. 1 Catalytic activity for NO_x reduction with propene (*a*) and conversion of propene into CO_2 (*b*) over the 25NbZ-P catalysts at various temperatures. Reaction conditions: 245 ppm NO_x ($NO/NO_2 = 1.77$), 504 ppm C_3H_6, 9 vol.% O_2, GHSV = 10,000 h^{-1})

empty IR cell (spectrum (a)). Gaseous NO_2 (band at 1,617 cm^{-1}) and N_2O_4 (bands at 1,758 and 1,264 cm^{-1}) are formed by the reaction of NO with O_2 in the gas phase ($2NO + O_2 = 2NO_2$). The concentrations of NO and NO_2 do not change appreciably after 30 min. The spectrum taken immediately after the exposure of the 25NbZ-P sample at room temperature to the same gas mixture (Fig. 2a, spectrum (b)), in addition to the absorptions of NO_2 and N_2O_4, contains a pair of bands at 1,832 and 1,305 cm^{-1} corresponding to the ν(N=O) and $\nu_s(NO_2)$ modes of asymmetric N_2O_3 [19]. Since the latter compound was not observed when mixing NO and O_2 in the empty IR cell (Fig. 2a, spectrum (a)), it is evident that the 25NbZ-P sample favors the comproportionation of NO and NO_2 to N_2O_3. The contact of the sample for 30 min with the gas mixture leads to strong increase in the amounts of NO_2 and N_2O_4 and significant lowering of the concentrations of NO and N_2O_3 (Fig. 2a, spectrum (c)). This result indicates that the 25NbZ-P sample promotes the oxidation of NO at room temperature. The spectra of the sample obtained immediately (Fig. 2b, spectrum (b)) and 30 min after the admission of the NO + O_2 mixture (Fig. 2b, spectrum (c)) contain bands at 1,900–1,885 and 1,755–1,752 cm^{-1} which are attributed to adsorbed N_2O_3 and N_2O_4, respectively [20, 21]. The broad absorption with maximum at 2,187 cm^{-1} is typical of NO^+ species [20–22]. The bands at 1,651, 1,217, and 1,004 cm^{-1} are assigned to the ν(N=O), $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ stretching vibrations of bridged nitrates, whereas the bands at 1,585, 1,270, and 1,020 cm^{-1} indicate the formation of bidentate NO_3^- species [20–22]. The shoulder at about 1,530 cm^{-1} (Fig. 2b, spectrum (c)) decreases in intensity during the outgassing (Fig. 2b, spectrum (d)). This absorption is due most likely to the $\nu_{as}(NO_2)$ mode of adsorbed N_2O_3 [20–22] which is superimposed to the ν(N=O) stretching vibration of a second bidentate nitrate. The $\nu_s(NO_2)$ modes of the latter species is positioned at 1,030 cm^{-1}, whereas the $\nu_{as}(NO_2)$ band should fall between 1,350 and 1,200 cm^{-1} and cannot be resolved. Since the Zr^{4+} ions are considered to be irreducible, the Nb^{5+} species should play the role of oxidizing centers in the processes of NO_2/N_2O_4 and surface

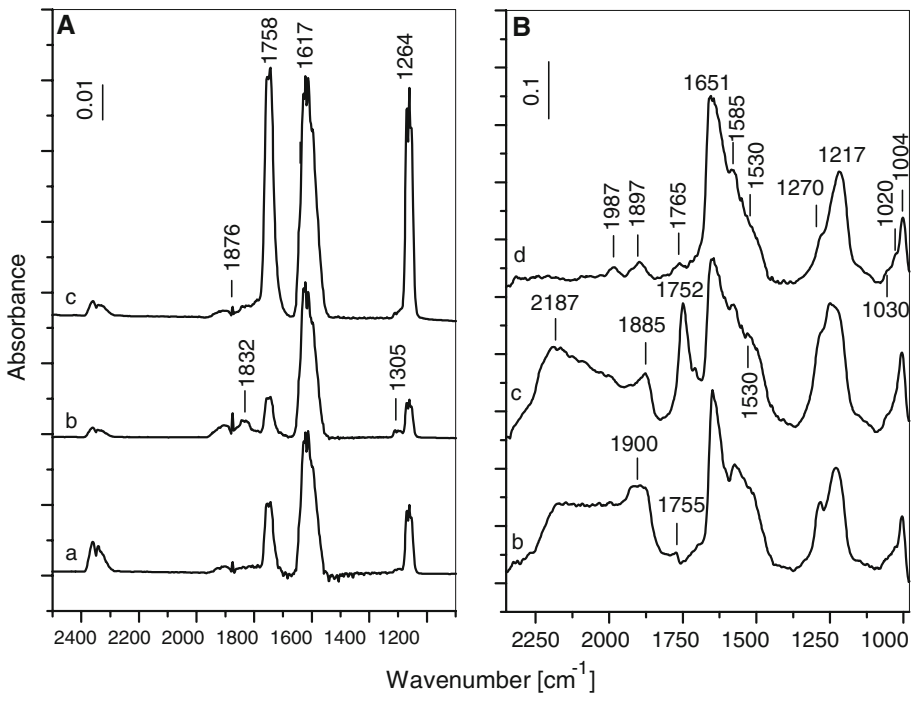


Fig. 2 **a** Gas phase spectra recorded at room temperature immediately after the admission of a (10 mbar NO + 20 mbar O_2) mixture to the empty IR cell (*a*), after the introduction of the same gas mixture immediately to the IR cell in the presence of the 25NbZ-P catalyst (*b*), and after 30 min (*c*). **b** FT-IR spectra of adsorbed NO_x species taken immediately during the exposure of the 25NbZ-P catalyst to the same gas mixture at room temperature (*b*), after 30 min (*c*) and upon dynamic evacuation for 30 min (*d*)

nitrate generation. Another possibility for the formation of surface NO_3^- species is through self-ionization of NO_2 on surface Lewis acid–base pairs according to the reaction [20–22]:

$$2NO_2 \rightarrow NO_3^- + NO^+$$

In general, the NO_2, N_2O_4, and N_2O_3 molecules are weakly adsorbed and they can be removed easily by evacuation [20–22]. Therefore, the weak bands at 1,987, 1,897, and 1,764 cm^{-1} observed in the spectrum upon prolonged evacuation (Fig. 2b, spectrum (d)) are attributed to combination modes of the nitrate species [20, 22]. The NO^+ species disappear upon the evacuation. The assignment of the absorption bands observed during the NO + O_2 coadsorption on the 25NbZ-P sample at room temperature is proposed in Table 1.

The thermal stability of the nitrate species adsorbed on the 25NbZ-P sample was investigated by heating the isolated IR cell in the 25–350 °C temperature range for 15 min at each temperature (Fig. 3). A gradual decrease in the intensities of the nitrate bands is observed with the increase in the temperature (Fig. 3a). At 350 °C the NO_3^- species almost vanish. The gas phase spectra (Fig. 3b) show that the product of thermal decomposition of the nitrates is NO_2. It should be noted that the thermal stability of surface nitrates formed on pure zirconia is significant higher that that of the nitrate species adsorbed on the 25NbZ-P sample. In the former case the NO_3^- species resist the dynamic evacuation at 400 °C and under these conditions they are present in significant amount on the surface of zirconia [22]. This indicates that the introduction of niobium(V) to zirconia lowers the thermal stability of the surface nitrates.

Table 1 Assignments of the absorption bands in the spectra observed during the NO + O_2 coadsorption on the 25NbZ-P catalyst at room temperature

Species	Band position (cm^{-1})	Vibration
NO^+	2,187	ν(NO)
N_2O_3(ads)	1,885	ν(N=O)
	1,530	$\nu_{as}(NO_2)$
N_2O_4(ads)	1,752	$\nu_{as}(NO_2)$
Bridged NO_3^-	1,651	ν(N=O)
	1,217	$\nu_{as}(NO_2)$
	1,004	$\nu_s(NO_2)$
	1,987, 1,897	$\nu_s(NO_2) + \delta$(ONO)
Bidentate NO_3^- (two types)	1,585, 1,530	ν(N=O)
	1,270	$\nu_{as}(NO_2)$
	1,020, 1,030	$\nu_s(NO_2)$
	1,765	$\nu_s(NO_2) + \delta$(ONO)

3.2.2 *Co-adsorption of (C_3H_6 + O_2) on the 25NbZ-P Catalyst*

Figure 4 shows the development of the spectra in the 25–350 °C temperature range obtained during the contact of the catalyst with a gas mixture containing 3 mbar of C_3H_6 and 10 mbar of O_2. The bands at 1,619 and 1,451 cm^{-1} observed in the spectrum detected at room temperature (Fig. 4, spectrum (a)) are characteristic of propene adsorbed on oxide surfaces and correspond to the ν(C=C) and $\delta_{as}(CH_3)$ modes, respectively [23]. The weak absorption at 2,980–2,950 cm^{-1} is assigned to the CH_3 stretching vibrations. Heating the closed IR cell at 100 °C for 15 min (Fig. 4, spectrum (b)), causes decrease in the intensity of the bands at 1,619 and 1,451 cm^{-1} of adsorbed propene and appearance of weak bands at 1,104 and 1,010 cm^{-1}. The shape of the absorption in the CH_3 stretching region has changed. At 150 °C (Fig. 4, spectrum (c)) the adsorbed propene disappears almost completely. The bands at 2,982 [$\nu_{as}(CH_3)$] and 2,936 cm^{-1} [$\nu_s(CH_3)$] detected under these conditions (Fig. 4, spectrum (c)) are characteristic of two types of isopropoxy species with the ν(C–O) modes at 1,104 and 1,010 cm^{-1}, respectively [24–30]. At 200 °C (Fig. 4, spectrum (d)), new absorptions at 1,669 and 1,560 cm^{-1} are observed. The former band is attributed to the ν(C=O) stretching of adsorbed acetone [25–28, 31] which is formed at the expense of the isopropoxy species. This assignment is supported by the observation that the activation of propene over catalysts containing Brønsted acid sites proceeds through formation of surface isopropoxides, which are transformed into acetone followed by oxidation of the latter molecule to acetate species [25, 26]—the weak band at 1,560 cm^{-1}. When the temperature is raised to 250 °C (Fig. 4, spectrum (e)), strong absorptions emerge at 1,590, 1,538, 1,444, and 1,410 cm^{-1} (shoulder), which are assigned to the COO stretching vibrations of two types of acetate species [26–28, 31]. The assignment of the absorption bands is summarized in Table 2.

3.2.3 *Reactivity of the Surface Species Formed upon Room-temperature Adsorption of NO + C_3H_6 + O_2 Mixture on the 25NbZ-P Catalyst*

The 25NbZ-P sample was exposed to a gaseous mixture containing 18 mbar NO + 3 mbar C_3H_6 + 10 mbar O_2 at room temperature for 20 min followed by evacuation for 10 min. The spectrum obtained under these conditions is shown in Figs. 5a, b, spectrum (a). The broad absorption between 3,600 and 2,500 cm^{-1} is typical of H-bonded hydroxyls and indicates that the oxidation of propene has occurred already at room temperature. The weak bands at 2,990 and 2,935 cm^{-1} are attributed to the $\nu_{as}(CH_3)$ and

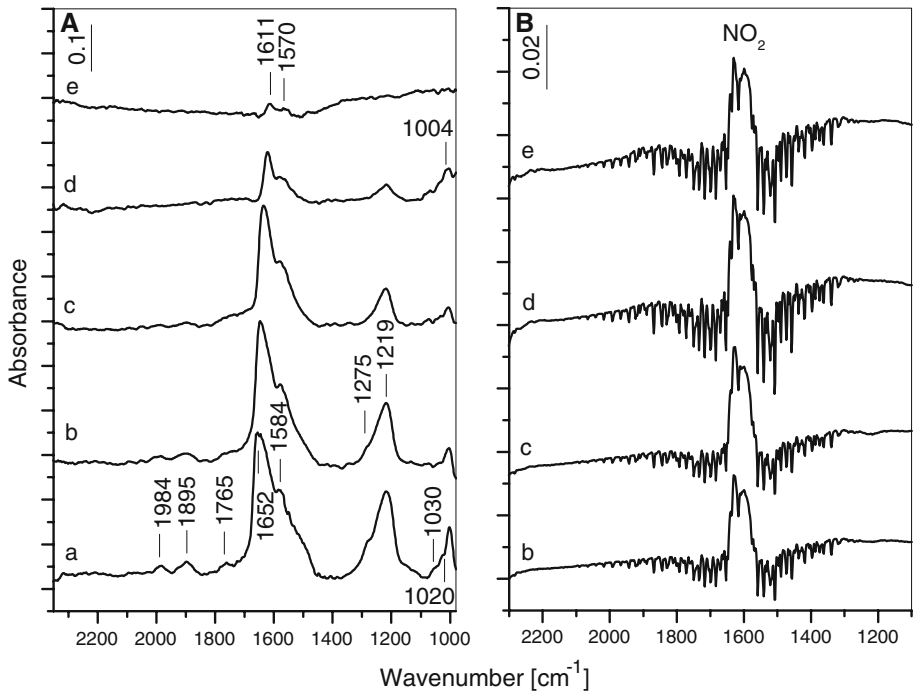


Fig. 3 **a** FT-IR spectra of the 25NbZ-P catalyst taken after the adsorption of a (10 mbar NO + 20 mbar O_2) mixture to the IR cell for 30 min at room temperature followed by evacuation for 30 min (*a*), and after heating the isolated IR cell for 15 min at 100 °C (*b*), 150 °C (*c*), 250 °C (*d*) and 350 °C (*e*). **b** Gas phase spectra collected at 100 °C (*b*), 150 °C (*c*), 250 °C (*d*) and 350 °C (*e*)

$\nu_s(CH_3)$ stretching vibrations of adsorbed propene and partially oxidized derivatives of the hydrocarbon. The bands in the 1,800–1,000 cm^{-1} region overlap heavily and it is difficult to propose an unambiguous assignment. Based on the spectra of adsorbed NO_3^- species (Fig. 2), the absorptions at 1,654, 1,234, 1,570, and 1,275 cm^{-1} are all assignable to bridged and bidentate nitrates. However, judging from the relative intensities of the nitrate bands at 1,275 and 1,234 cm^{-1}, it seems that the population of the bidentate nitrates at 1,570 and 1,275 cm^{-1} formed in the NO + C_3H_6 + O_2 experiment is higher than that generated during the NO + O_2 co-adsorption (compare with Fig. 2). This indicates that there is a competition between the nitrate species and other surface compounds for the same adsorption sites. The absorption at 1,610 cm^{-1} can be attributed to both bending mode of adsorbed water and $\nu_{as}(COO)$ stretching vibration of adsorbed acetate [26–28, 31]. Most likely, two types of acetate species are formed which is supported by the presence of two bands at 1,454 and 1,420 cm^{-1} corresponding to their $\nu_s(COO)$ modes [26–28, 31]. The $\nu_{as}(COO)$ stretching vibration of the second acetate species is probably covered by the nitrate band at 1,570 cm^{-1}. The absorption at 1,725 cm^{-1} is characteristic of a carbonyl moiety and is attributed to nitroacetone. Arguments for this assignment are given below. Here it should be noted that nitroketones exhibit absorptions at 1,730, 1,560, and 1,380 cm^{-1} corresponding to the ν(C=O), $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ modes [32]. The antisymmetric NO_2 stretching vibration of nitroacetone is covered by the nitrate band at 1,570 cm^{-1} and cannot be resolved. The band at 1,139 cm^{-1} is assigned to the δ(CCC) mode of the nitroketone. The weak absorptions at 1,098 and 1,010 cm^{-1} are attributed to the ν(C–O) modes of adsorbed isopropoxides [24–30]. The latter absorption has a contribution from the $\nu_s(NO_2)$ stretching vibration of the bridged nitrates. The broad band at 2,290 cm^{-1} is typical of NCO species adsorbed on oxide surfaces [33–38]. An argument in support of the assignment of the absorption at 2,290 cm^{-1} to a N,C-containing species is the absence of this feature in the spectra obtained during the NO + O_2 coadsorption (see Fig. 2b, spectrum (d) and Fig. 3a). The formation of NCO species could be associated with the transformation of nitroacetone. Weingand et al. [38] observed generation of –C=O-containing compounds at 100 °C during the interaction between propene and nitrate species adsorbed on WO_3–ZrO_2. They suggested that the –C=O-containing species are converted into isocyanates with the participation of surface nitrates.

Finally, the fact that no partially oxidized hydrocarbon species were observed at room temperature during the C_3H_6 + O_2 experiment (Fig. 4, spectrum (a)), indicates that the formation of surface nitrates and/or gaseous NO_2 during the room-temperature adsorption of NO + C_3H_6 + O_2 mixture facilitates the activation of propene.

Heating the sample for 15 min at 100 °C causes the following changes:

(1) Increase in the concentrations of partially oxidized hydrocarbons (Fig. 5b, spectrum (b)), which is evident by the enhancement of the intensities of the bands corresponding to the isopropoxides (1,098 cm^{-1}), acetates

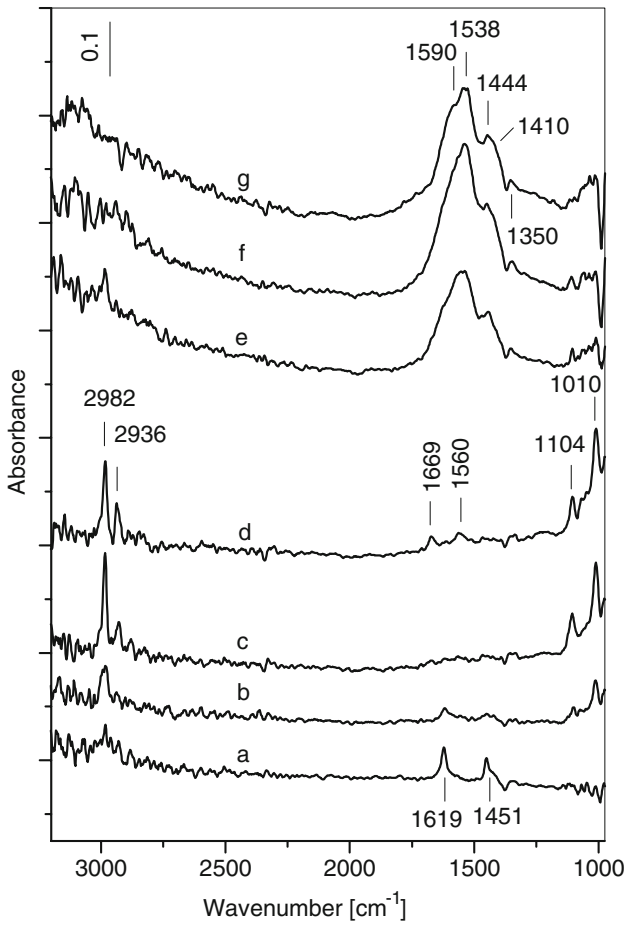


Fig. 4 FT-IR spectra collected during the exposure of the 25NbZ-P catalyst to a (3 mbar C_3H_6 + 10 mbar O_2) mixture for 15 min at room temperature (*a*) followed by heating the isolated IR cell for 15 min at 100 °C (*b*), 150 °C (*c*), 200 °C (*d*), 250 °C (*e*), 300 °C (*f*) and 350 °C (*g*)

Table 2 Assignments of the adsorption bands in the spectra observed during the high-temperature adsorption of C_3H_6 + O_2 mixture on the 25NbZ-P catalyst

Species	Band position (cm^{-1})	Vibration
C_3H_6 (ads)	1,619	ν(C=C)
	1,451	$\delta_{as}(CH_3)$
Isopropoxide (two types)	2,982, 2,936	$\nu_{as}(CH_3)$, $\nu_s(CH_3)$
	1,104, 1,010	ν(C–O)
Acetone (ads)	1,669	ν(C=O)
CH_3COO^- (two types)	1,590, 1,560–1,538	ν_{as}(COO)
	1,410, 1,444	ν_s(COO)
	1,350	$\delta(CH_3)$

(1,454 and 1,420 cm^{-1}) and nitroacetone (1,725 and 1,139 cm^{-1}). This is accompanied by the appearance of a pronounced absorption at 2,880 cm^{-1} typical of CH_2 stretching vibration (Fig. 5a, spectrum (b)). The fact that there is enhancement in the concentration of partially oxidized hydrocarbons (isopropoxides, nitroacetone, acetates) at 100 °C suggests the presence of adsorbed propene at room temperature.

(2) Decrease in the concentration of the surface nitrates and isocyanates (the ν_{as}(NCO) band is shifted to 2,260 cm^{-1}) which is accompanied by formation of NO_2 and N_2O in the gas phase (Fig. 5c, spectrum (b)).

At 150 °C (Fig. 5b, spectrum (c)), the nitrate bands at 1,275 and 1,234 cm^{-1} almost vanished, which is accompanied by strong decrease in the concentration of gaseous NO_2 (Fig. 5c, spectrum (c)) and increase in the amount of CO_2 and N_2O. The intensities of the bands at 1,139 and 1,098 cm^{-1} (Fig. 5b, spectrum (c)) associated with the adsorbed nitroacetone and isopropoxide are reduced and they appear as unresolved absorption between 1,160 and 1,070 cm^{-1}. The weak band at 1,050 cm^{-1} is assigned to the $\rho(CH_3)$ mode of the acetate species [27] whose concentration has increased significantly. The latter is evident by the observed increase in the intensities of the bands at 1,454 and 1,420 cm^{-1} corresponding to the ν_s(COO) stretching vibrations of the acetates. The absorption at 1,684 cm^{-1} is characteristic of the ν(C=O) mode of acetone coordinated to a Lewis acid site [25–28, 31]. This assignment is supported by the spectra of acetone adsorbed between 25 and 350 °C (see below). Most likely, the acetone is formed below 150 °C simultaneously with the nitroacetone but the strong nitrate band at 1,654 cm^{-1} hinders the detection of the former compound. The amount of the NCO species detected under these conditions is extremely low (Fig. 5b, traces (c) and (cx2)). The changes in the spectrum taken at 200 °C (Fig. 5b, spectrum (d)) are associated with small decrease in the intensities of the absorption bands due to nitroacetone and acetone which is evident from the subtraction spectrum (d–c). This spectrum is not shown. No appreciable amount of NCO species is detected under these conditions. It should be noted that at 200 °C, NO_2 disappears from the gas phase. There is some increase in the amount of CO_2 (Fig. 5c, spectrum (d)).

Between 250 and 300 °C (Fig. 5b, spectra (d) and (f)) the predominant surface species are the acetates. The surface nitrates, acetone and nitroacetone disappear at 250 °C (Fig. 5b, spectrum (e)). Further increase in the temperature results in gradual decomposition of the acetate species which is accompanied by increase in the concentration of CO_2 and formation of small amount of CO in the gas phase (Fig. 5c, spectra (e) to (g)). At 350 °C, CO disappears and N_2O is detected in lower concentration. The assignment of the absorption bands observed during the interaction of the species obtained by room-temperature adsorption of NO + O_2 + C_3H_6 mixture over the 25NbZ-P catalyst is summarized in Table 3.

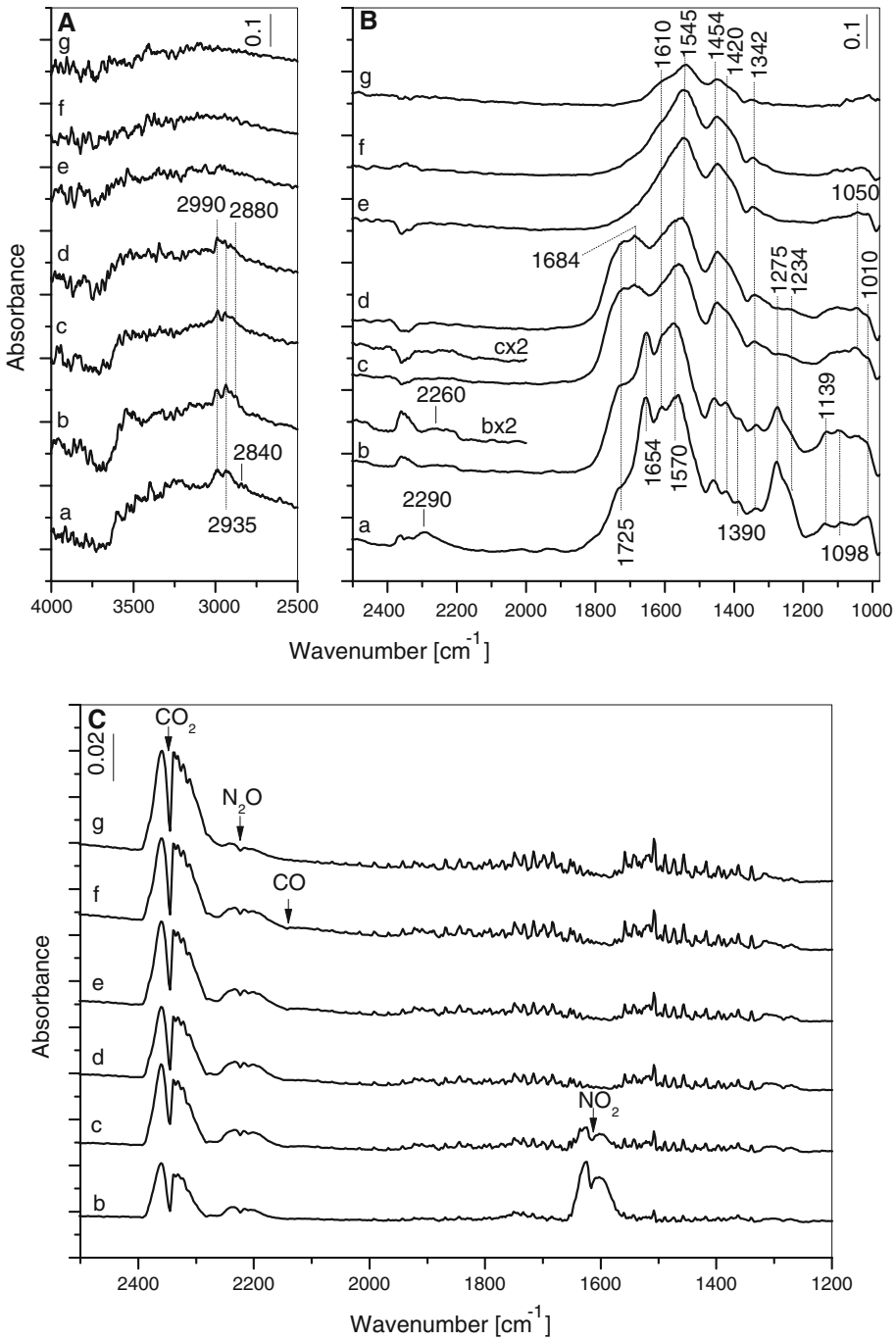


Fig. 5 FT-IR spectra collected during the exposure of the 25NbZ-P catalyst to a (18 mbar NO + 3 mbar C_3H_6 + 10 mbar O_2) mixture at room temperature for 20 min followed by evacuation for 10 min (*a*) and heating the isolated IR cell for 15 min at 100 °C (*b*), 150 °C (*c*), 200 °C (*d*), 250 °C (*e*), 300 °C (*f*) and 350 °C (*g*). FT-IR spectra of the catalyst recorded in the 4,000–2,500 cm^{-1} region (Panel **a**), 2,500–980 cm^{-1} region (Panel **b**) and gas phase spectra (Panel **c**)

The disappearance of NO_2 from the spectrum taken at 200 °C is in strong contrast with the results of the thermal stability of the nitrate species in the absence of propene (see Fig. 3). In the latter experiment gaseous NO_2 was observed in the whole temperature range between 100 and 350 °C. This difference suggests that the NO_3^- species, respectively activated NO_2 surface complex, react with the adsorbed propene and/or hydrocarbon oxygenates.

3.2.4 Adsorption of Acetone and its Interaction with NO_2 Over the 25NbZ-P Catalyst

In order to confirm the assignment of the absorption band at 1,725 cm^{-1} (Fig. 5b) to adsorbed nitroacetone, we investigated the adsorption of acetone and its interaction with NO_2 at elevated temperatures.

The adsorption of 1 mbar of acetone on the 25NbZ-P sample at room temperature followed by evacuation for

Table 3 Assignment of the absorption bands observed during the investigation of the reactivity of surface species formed upon room-temperature adsorption of NO + C_3H_6 + O_2 mixture on the 25NbZ-P catalyst in the 25–350 °C temperature range

Species	Band position (cm^{-1})	Vibration
Isopropoxide (two types)	2,990, 2,935	$\nu_{as}(CH_3)$, $\nu_s(CH_3)$
	1,098, 1,010	ν(C–O)
Acetone (ads)	2,990, 2,935	$\nu_{as}(CH_3)$, $\nu_s(CH_3)$
	1,684	ν(C=O)
	1,139	δ(CCC)
Nitroacetone (ads)	2,990, 2,935	$\nu_{as}(CH_3)$, $\nu_s(CH_3)$
	2,880	$\nu(CH_2)$
	1,725	ν(C=O)
	1,139	δ(CCC)
Bridged NO_3^-	1,654, 1,234, 1,010	ν(N=O), $\nu_{as}(NO_2)$, $\nu_s(NO_2)$
Bidentate NO_3^-	1,570, 1,275, 1,010	ν(N=O), $\nu_{as}(NO_2)$, $\nu_s(NO_2)$
CH_3COO^- (two types)	1,610, 1,545	ν_{as}(COO)
	1,420, 1,454	ν_s(COO)
	1,342, 1,050	$\delta(CH_3)$, $\rho(CH_3)$
NCO	2,290	ν_{as}(NCO)

15 min, results in spectrum (a) shown in Fig. 6. The strong band at 1,687 cm^{-1} corresponds to the ν(C=O) stretching vibration of adsorbed acetone [25–28, 31]. This band is red-shifted as compared with the ν(C=O) stretching vibration of gaseous acetone and indicates that the molecule is coordinated to a Lewis acid site [25]. The intensities

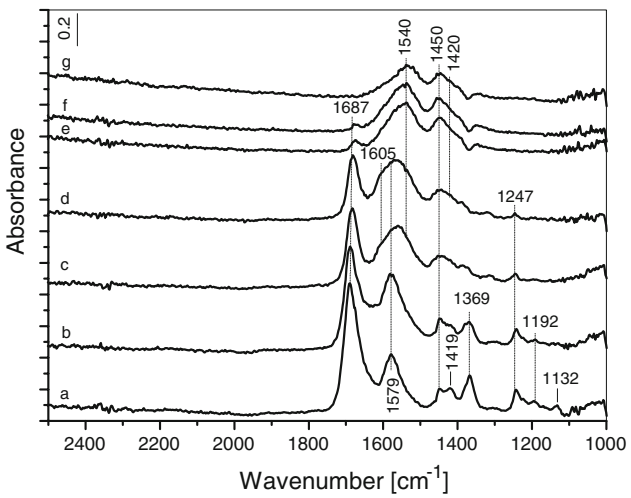


Fig. 6 FT-IR spectra of acetone (1 mbar) adsorbed on the 25NbZ-P catalyst for 10 min at room temperature followed by evacuation for 10 min (*a*) and after heating the isolated IR cell for 15 min at 100 °C (*b*), 150 °C (*c*), 200 °C (*d*), 250 °C (*e*), 300 °C (*f*) and 350 °C (*g*)

of the bands at 1,419, 1,369, 1,247, 1,192, and 1,132 cm^{-1} decrease with the temperature simultaneously with the absorption at 1,687 cm^{-1}. Therefore, all these bands are attributed to various vibrational modes of the adsorbed acetone (see Table 4). The bands at 1,579 and 1,450 cm^{-1} observed in spectrum (a) are best assigned to bidentate acetates and correspond to the ν_{as}(COO) and ν_s(COO) modes, respectively [26–28, 31]. This experimental fact indicates that the 25NbZ-P catalyst is able to oxidize the adsorbed acetone already at room temperature. Heating the isolated IR cell for 15 min at 100 °C, leads to increase in the amount of the acetates at 1,579 and 1,450 cm^{-1} at the expense of adsorbed acetone (Fig. 6, spectrum (b)). At 150 (spectrum (c)) and 200 °C (spectrum (d)), the population of the CH_3COO^- species grows further. This is evident by the appearance of poorly resolved absorptions at approximately 1,604 and 1,540 cm^{-1} assigned to the ν_{as}(COO) modes of two new acetate species. The oxidation of acetone occurs in great extent at temperatures higher than 200 °C which is evident by the significant increase in the concentration of the acetate species at 250 °C (Fig. 6, spectrum (e)). The heating at 350 °C (spectrum (g)) does not lead to their complete removal, the acetates at 1,540 cm^{-1} being the most stable. Adsorbed acetone is observed up to 300 °C (spectrum (f)). The assignment of the absorption bands is summarized in Table 4.

Table 4 Assignments of the absorption bands in the spectra observed during the high-temperature adsorption of acetone and its coadsorption with NO_2 on the 25NbZ-P catalyst

Species	Band position (cm^{-1})	Vibration
Acetone (ads)	2,985, 2,925	$\nu_{as}(CH_3)$, $\nu_s(CH_3)$
	1,690–1,687	ν(C=O)
	1,419–1,417	$\delta_{as}(CH_3)$
	1,370–1,369	$\delta_s(CH_3)$
	1,247, 1,192	ν_{as}(CCC), ν_s(CCC)
	1,139	δ(CCC)
Nitroacetone (ads)	2,985, 2,925	$\nu_{as}(CH_3)$, $\nu_s(CH_3)$
	2,885	$\nu(CH_2)$
	1,735	ν(C=O)
	1,130	δ(CCC)
Bridged NO_3^-	1,660, 1,250, 1,010	ν(N=O), $\nu_{as}(NO_2)$, $\nu_s(NO_2)$
Bidentate NO_3^-	1,573, 1,276, 1,010	ν(N=O), $\nu_{as}(NO_2)$, $\nu_s(NO_2)$
Bidentate CH_3COO^- (two types)	1,615–1,579, 1,540	ν_{as}(COO)
	1,417–1,410, 1,453–1,450	ν_s(COO)
	1,350	$\delta(CH_3)$
NCO	2,260	ν_{as}(NCO)

The spectra shown in Fig. 7 are obtained during the interaction of NO_2 in the 25–350 °C temperature range with acetone adsorbed at room temperature on the surface of the 25NbZ-P sample. The activated sample was left in contact with 1 mbar of acetone for 10 min at room temperature followed by evacuation for 10 min. Then to the IR cell 1.4 mbar of NO_2 were added and the isolated IR cell containing gaseous NO_2 was heated between 25 and 350 °C for 15 min at each temperature. The spectrum detected at room temperature (Fig. 7a, spectrum (a)) contains bands at 2,985 and 2,925 cm^{-1} due to the $\nu_{as}(CH_3)$ and $\nu_s(CH_3)$ modes of adsorbed acetone. The latter compound gives rise to the bands at 1,690 (ν(C=O)), 1,417 ($\delta_{as}(CH_3)$) and 1,370 cm^{-1} ($\delta_s(CH_3)$) in the 1,700–1,000 cm^{-1} region (Fig. 7b, spectrum (a)). The weak absorption at 1,453 cm^{-1} suggests formation of

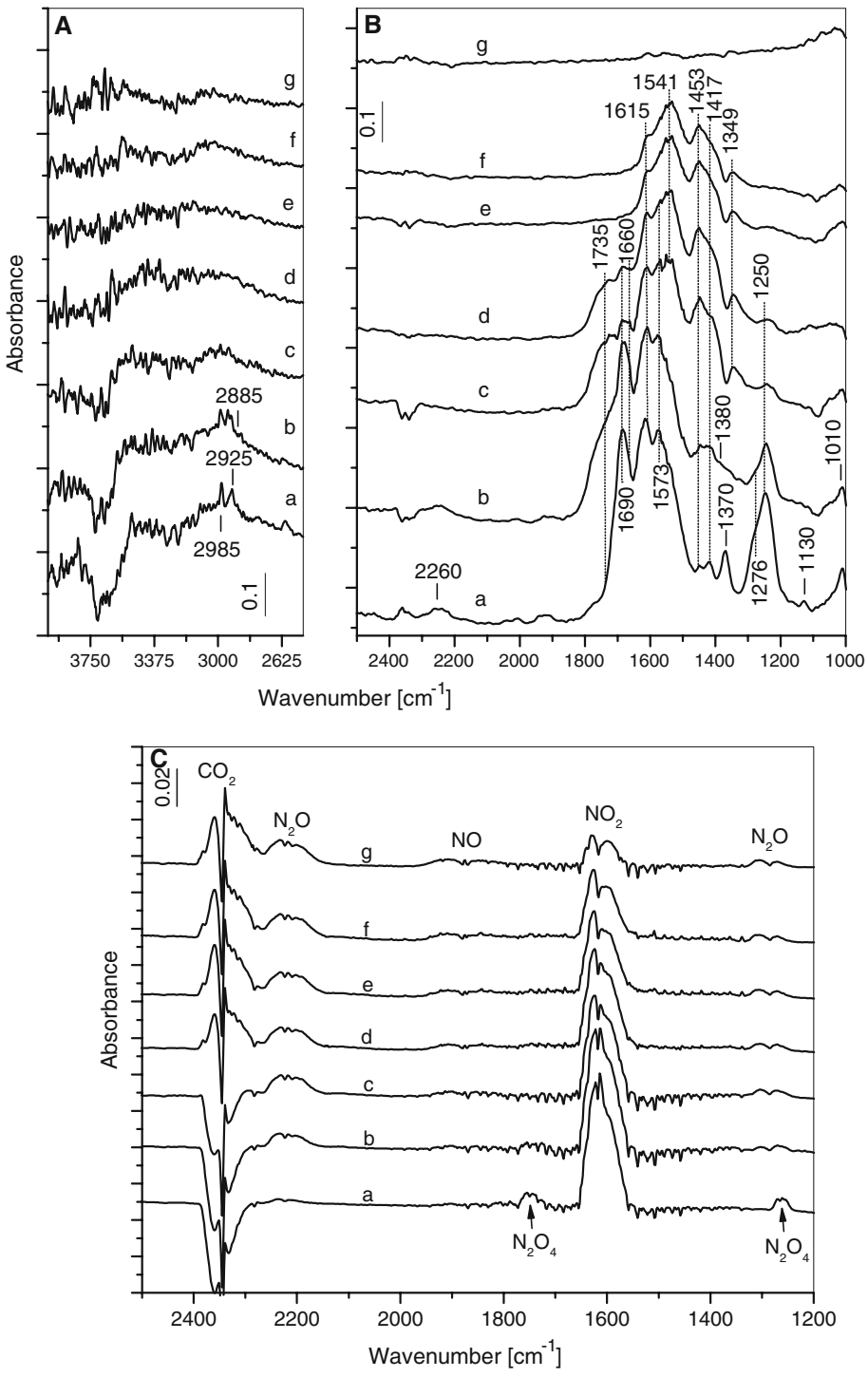


Fig. 7 FT-IR spectra of adsorbed acetone (1 mbar) on the 25NbZ-P catalyst for 10 min at room temperature followed by evacuation for 10 min and addition of 1.4 mbar NO_2 (*a*) and heating the isolated IR cell for 15 min at 100 °C (*b*), 150 °C (*c*), 200 °C (*d*), 250 °C (*e*), 300 °C (*f*) and 350 °C (*g*). FT-IR spectra of the catalyst recorded in the 4,000–2,500 cm^{-1} region (Panel **a**) and 2,500–1,000 cm^{-1} region (Panel **b**) and gas phase spectra (Panel **c**)

acetate species and is attributed to the ν_s(COO) mode. As shown above, the bands at 1,660 and 1,250 cm^{-1} and at 1,573 and 1,276 cm^{-1} are due mainly to bridged and bidentate nitrate species (ν(N=O) and $\nu_{as}(NO_2)$ modes). Weak band with maximum at 2,260 cm^{-1} and shoulder at approximately 1,735 cm^{-1} are detected. As in the case of adsorbed acetone in the absence of NO_2 (Fig. 6), the increase in the temperature to 100 °C causes increase in the amount of acetate species, which is evident by the enhancement of the intensities of the bands at 1,453 and 1,417 cm^{-1} (Fig. 7b, spectrum (b)). In addition, there is a strong increase of the absorption at 1,735 cm^{-1} and decrease in the intensity of the band at 2,260 cm^{-1}. The latter two bands are not observed during the adsorption of acetone in the absence of NO_2 (see Fig. 6). This confirms the assumption made above that the absorption at 1,735 cm^{-1} corresponds to nitroacetone and its transformation leads to the generation of NCO species giving rise to the absorption at 2,260 cm^{-1}. The formation of nitroacetone from acetone is supported by the observed strong decrease in the intensity of the band at 1,370 cm^{-1} due to the $\delta_s(CH_3)$ mode of adsorbed acetone (Fig. 7b, spectrum (b)) and appearance of a pronounced shoulder at 2,885 cm^{-1} corresponding to the $\nu(\nu CH_2)$ stretching vibration (Fig. 7a, spectrum (b)). This indicates that substitution of hydrogen atom(s) in the methyl group(s) of acetone for nitro group(s) has occurred.

The development of the absorption bands between 150 and 350 °C is analogous to that observed during the adsorption of NO + C_3H_6 + O_2 mixture on the surface of the 25NbZ-P catalyst (compare with Fig. 5b). However, no NCO species are detected at 150 °C in the presence of gaseous NO_2 (compare spectra (c) in Figs. 5b, 7b). The acetone and its nitro substituent disappear from the surface of 25NbZ-P sample at 250 °C (Fig. 7b, spectrum (e)). The spectra detected at this temperature and 300 °C (spectrum (f)) contain bands due mainly to adsorbed acetate species (1,615, 1,541, 1,453, 1,417, and 1,349 cm^{-1}). The decomposition of surface acetates begins at 250 °C, which causes decrease in their concentration and disappearance at 350 °C. The spectra of the gas phase taken between 25 and 350 °C are shown in Fig. 7c. The amount of NO_2 gradually decreases with the temperature which could be attributed to shift of the equilibrium $NO_2 \leftrightarrow NO + 0.5O_2$ to the right and interaction of NO_2 with the adsorbed acetone, nitroacetone and NCO species. The latter processes account for the formation of significant amount of CO_2 at 200 °C (Fig. 7c, spectrum (d)).

Table 4, 5 summarizes the assignment of the absorption bands observed in the spectra detected during the adsorption of acetone and its co-adsorption with NO_2 on the 25NbZ-P sample.

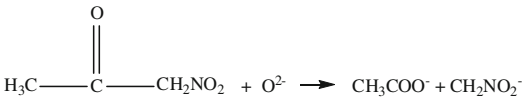
Table 5 Assignment of the absorption bands observed during the investigation of the reactivity of surface species formed upon room-temperature adsorption of NO + C_3H_6 + O_2 mixture on the 0.1Pd/25NbZ-P catalyst in the 25–350 °C temperature range

Species	Band position (cm^{-1})	Vibration
Isopropoxide (two types)	2,990, 2,930	$\nu_{as}(CH_3)$, $\nu_s(CH_3)$
	1,094, 1,010	ν(C–O)
Acetone (ads)	2,990, 2,930	$\nu_{as}(CH_3)$, $\nu_s(CH_3)$
	1,686	ν(C=O)
	1,332, 1,138	$\delta_s(CH_3)$, δ(CCC)
Nitroacetone (ads)	2,990, 2,930	$\nu_{as}(CH_3)$, $\nu_s(CH_3)$
	1,730	ν(C=O)
	1,332, 1,138	$\delta_s(CH_3)$, δ(CCC)
Bridged NO_3^-	1,656, 1,250, 1,010	ν(N=O), $\nu_{as}(NO_2)$, $\nu_s(NO_2)$
Bidentate NO_3^-	1,573, 1,279, 1,010	ν(N=O), $\nu_{as}(NO_2)$, $\nu_s(NO_2)$
CH_3COO^- (two types)	1,593, 1,553	ν_{as}(COO)
	1,457, 1,422	ν_s(COO)
	1,346, 1,053	$\delta(CH_3)$, $\rho(CH_3)$
NCO/$Zr_6Nb_2O_{17}$	2,290	ν_{as}(NCO)
Pd-NCO	2,182	ν_{as}(NCO)

4 Discussion

The FT-IR spectra obtained during the adsorption of (NO + C_3H_6 + O_2) and (acetone + NO_2) mixtures on the 25NbZ-P catalyst show formation of NCO species already at room temperature. The surface isocyanates are considered to be reactive intermediates in the selective reduction of NO_x with hydrocarbons [4–6, 39–46]. In the case of supported copper catalysts, which are among the most active non-noble metal oxide catalysts in the selective reduction of NO_x with propene, the formation of NCO species is detected at higher temperatures (150–250 °C) [34, 39, 42, 43, 47–49]. Their generation through transformation of organic nitro compound, $C_xH_yNO_z$, has been proposed for various catalytic systems [4–6, 35–37, 40, 43, 46, 48–53]. Our experiments with nitropropane show that this compound immediately isomerizes to nitritopropane upon adsorption on the 25NbZ-P sample at room temperature (the spectra are not shown). The heating between 100 and 350 °C causes the oxidation of the adsorbed nitritopropane to surface acetates and above 200 °C the spectra contain only the characteristic bands of the latter species. No NCO groups are detected in the whole temperature range. Therefore, it can be proposed that the source of isocyanates over the 25NbZ-P sample is the nitroacetone. Pearson et al. [54] have shown that in a weak basic medium nitroacetone produces aci-anion of nitromethane ($CH_2NO_2^-$) and acetate species. The former

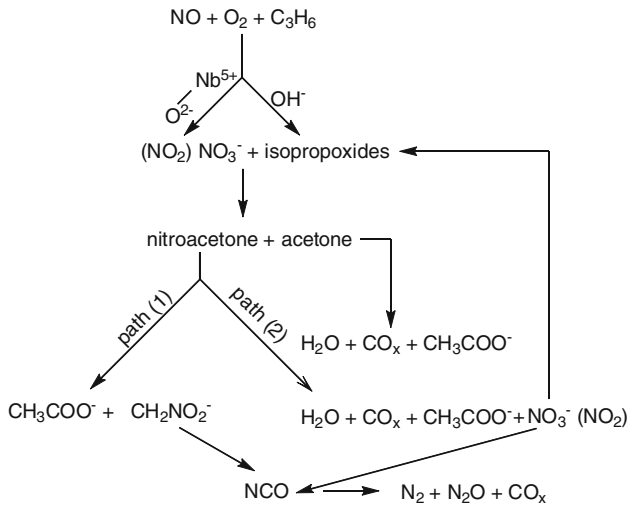
compound in turn can transform into NCO groups [4, 37, 46, 52, 53]. Most likely, the decomposition of nitroacetone to aci-nitromethane and CH_3COO^- species occurs on basic O^{2-} sites of the 25NbZ-P sample:



(1)

The characteristic vibrations of aci-nitromethane fall in the 1,650–1,200 cm^{-1} region [37, 52, 53] and if they are present, they cannot be located due to overlapping with the nitrate-carboxylate bands. However, the product of aci-nitromethane transformation, the NCO species, is clearly observable at 2,290–2,260 cm^{-1} in the spectra taken at 25 and 100 °C (Figs. 5b, 7b, spectra (a) and (b)). It is well known that the surface isocyanates react easily with NO + O_2 mixtures and/or NO_2 yielding molecular nitrogen and N_2O as reaction products [4–6, 34, 35, 38, 41, 43, 50]. This fact can account for the disappearance of the NCO species and NO_2 at temperatures higher than 100–150 °C. Therefore, we are of the opinion that the low-temperature activity the 25NbZ-P catalyst is associated with the nature of the organic nitro compound formed during the course of the reaction. Most probably the transformation route of nitropropane to isocyanate species over the majority of oxide-based catalysts is energetically more expensive than that of nitroacetone via aci-nitromethane to NCO as proposed for the 25NbZ-P catalyst.

The experimental results show that the nitroacetone and acetone disappear simultaneously at 250 °C (Figs. 5b, 7b, spectrum (e)). It can be proposed that under these conditions both compounds are further oxidized to acetates. The latter species begin to decompose at 250 °C causing an increase in the amount of CO_2 (Figs. 5c, 7c, spectrum (e)). It seems that the nitroacetone and acetone have the same thermal stability when adsorbed on the 25NbZ-P catalyst. As shown above, the oxidation of adsorbed acetone to CH_3COO^- species occurs in large extent at 250 °C (see Fig. 6). In other words, we assume that the nitroacetone can undergo transformations through two parallel reactions: path (1) consisting of acid–base reaction (reaction 1) and path (2) involving the oxidation of nitroacetone. The latter process is important most likely at temperatures higher than 200 °C. The products of high-temperature transformation of nitroacetone would be NO_x species, presumably NO_2 or surface nitrate, in addition to the acetates and CO_x/H_2O. The NO_2/NO_3^- surface complex formed in path (2) can be involved in interactions with propene and/or surface isocianates.



Scheme 1

A mechanism for the surface reaction of propene and NO_x species adsorbed on the 25NbZ-P catalyst, deduced from the in situ FT-IR measurements, is proposed in Scheme 1.

It is assumed that the interaction of the isopropoxide species with the surface nitrates or/and activated NO_2 generates the nitroacetone. It should be noted that it is difficult to present direct evidence that the NCO species react with the surface NO_3^-/NO_2 complexes. The experimental results show that the NCO species are somewhat more stable in the absence of gaseous NO_2 and they produce a very weak band between 2,300 and 2,150 cm^{-1} at 150 °C (Fig. 5b, spectrum (c)). This absorption is absent in the spectrum taken at 150 °C upon NO_2 atmosphere (Fig. 7b, spectrum c) implying that the isocyanates react with NO_2 or activated NO_2 surface complex. Although the experimental conditions of the FT-IR investigation and catalytic test are different, it can be proposed that the nitroacetone and isocyanates could be the main reaction intermediates. This is supported by the facts that the NCO consumption is observed by in situ FT-IR spectroscopy already at 100 °C and the NO_x reduction over the 25NbZ-P catalyst with propene is significant at 180 °C (~30% of NO_x conversion). This assumption is in agreement with the currently accepted general mechanism of HC-SCR of NO_x [4–6] in which the participation of NCO species formed via organo-nitrogen compound is observed more readily under static conditions [35].

5 Conclusions

We have investigated the potential of niobium-zirconium mixed oxide as low-temperature catalysts for the SCR of NO_x with propene in excess oxygen. The mixed oxide was

prepared by impregnation of hydrated zirconia with acidic solution (pH 0.5) of peroxoniobium(V) complex, $[Nb_2(O_2)_3]^{4+}$, ensuring ZrO_2:Nb_2O_5 mole ratio of 6:1. The calcined sample (denoted as 25NbZ-P) has the structure of $Zr_6Nb_2O_{17}$. According to the catalytic test, the conversion of NO_x over the 25NbZ-P catalyst passes through a maximum at 220 °C. The results of detailed in situ FT-IR investigation have shown that over the 25NbZ-P sample, characterized by strong Brønsted acidity, the activation of propene in the presence of adsorbed NO_x species is quite easy at low temperatures, producing surface isopropoxides. The interaction of the latter species with the surface nitrate complexes leads to the formation of nitroacetone. It is proposed that nitroacetone transforms through two parallel reactions: (1) with the involvement of basic oxide sites of the catalyst producing acetate species and aci-nitromethane (path (1)) and (2) oxidation to acetates and CO_x/H_2O with release of NO_2 (path (2)). The latter process is important at temperatures higher than 200 °C. The aci-nitromethane generates NCO species coordinated to the cationic sites of the mixed oxide. The surface isocyanates are detected already at room temperature. It is proposed that the isocyanates react with the NO_3^-/NO_2 surface complex formed by both oxidation of NO and oxidation of nitroacetone. The facts that the NCO consumption is observed by in situ FT-IR spectroscopy already at 100 °C and the NO_x reduction over the 25NbZ-P catalyst is significant at 180 °C suggest that the nitroacetone and isocyanates could be the main reaction intermediates. The results of the investigation show that the catalytic properties of the $Zr_6Nb_2O_{17}$ solid solution could be of interest regarding the development of noble metal-free, low-temperature catalyst for the SCR of NO_x with hydrocarbons.

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References

1. Heck RM, Farrauto RJ (2001) Appl Catal A 221:443
2. Kaŝpar J, Fornasiero P, Hickey N (2003) Catal Today 77:419
3. Iwamoto M (2000) In: Corma A, Melo FV, Mendioroz S, and Fierro JLG (Eds) Stud Surf Sci Catal 130: 23
4. Burch R, Breen JP, Meunier FC (2002) Appl Catal B 39:283
5. Burch R (2004) Catal Rev–Sci Eng 46:271
6. Kung MC, Kung HH (2004) Top Catal 28:105
7. Nowak I, Ziolek M (1999) Chem Rev 99:3603
8. Tanabe K (2003) Catal Today 78:65
9. Mitadera J, Hinode H (2002) Appl Catal B 39:205
10. Kawai H, Hinode H (2008) React Kinet Catal Lett 93:67
11. Kikuchi T, Kumagai M (2001) J Japan Petr Inst 44:145
12. Kikuchi T, Kumagai M (2001) J Japan Petr Inst 44:340
13. Abdel-Rehim MA, dos Santos ACB, Camorim VLL, da Costa Faro A Jr (2006) Appl Catal A 305:211
14. Sobczak I, Ziolek M, Nowacka M (2005) Microp Mesopor Mater 78:103
15. Goscianska J, Bazin P, Marie O, Daturi M, Sobczak I, Ziolek M (2007) Catal Today 119:78
16. Goscianska J, Ziolek M (2008) Catal Today 137:197
17. Kantcheva M, Budunoglu H, Samarskaya O (2008) Catal Commun 9:874
18. Mestres L, Martinez-Sarrion ML, Catano O, Fernandez-Urban J (2001) Z Anorg Allg Chem 627:294
19. Laane J, Ohlsen JR (1986) Progr Inorg Chem 28:465
20. Kantcheva M, Cayirtepe I (2006) J Mol Catal A 247:88
21. Hadjiivanov KI (2000) Catal Rev–Sci Eng 42:71
22. Kantcheva M, Ciftlikli EZ (2002) J Phys Chem B 106:3941
23. Busca G, Ramis G, Lorenzelli V, Janin A, Lavalley JC (1987) Spectrochim Acta 43A:489
24. Rossi PF, Busca G, Lorenzelli V, Saur O, Lavalley JC (1987) Langmuir 3:52
25. Sanchez Escribano V, Busca G, Lorenzelli V (1990) J Phys Chem 94:8939
26. Finocchio E, Busca G, Lorenzelli V, Sanchez Escribano V (1996) J Chem Soc Faraday Trans 92:1587
27. Finocchio E, Willey RJ, Busca G, Lorenzelli V (1997) J Chem Soc Faraday Trans 93:175
28. Busca G, Finocchio E, Lorenzelli V, Ramis G, Baldi M (1999) Catal Today 49:453
29. Toda Y, Ohno T, Hatayama F, Miyata H (1999) Phys Chem Chem Phys 1:1615
30. Zaki MI, Hasan MA, Pasupulety L (2001) Langmuir 17:4025
31. Hasan MA, Zaki MI, Pasupulety L (2003) Appl Catal A 243:81
32. Adams LL, Luzzio FA (1989) J Org Chem 54:5387
33. Solymosi F, Bánsági T (1979) J Phys Chem 83:552
34. Ukisu Y, Sato S, Muramatsu G, Yoshida K (1992) Catal Lett 16:11
35. Haneda M, Kinaichi Y, Inaba M, Hamada H (1998) Catal Today 42:127
36. Satsuma A, Cowan AD, Cant NW, Trimm DL (1999) J Catal 181:165
37. Yamaguchi M (1997) J Chem Soc Faraday Trans 93:3581
38. Weingand T, Kuba S, Hadjiivanov K, Knözinger H (2002) J Catal 209:539
39. Li C, Bethke KA, Kung HH and Kung MC (1995) J Chem Soc—Chem Commun 813
40. Okuhara T, Yasada H, Misono M (1997) Catal Today 35:83
41. Sumiya S, He H, Abe A, Takezawa N, Yoshida K (1998) J Chem Soc Faraday Trans 94:2217
42. Shimizu K, Kawabata H, Maeshima H, Satsuma A, Hattori T (2000) J Phys Chem B 104:2885
43. Chi Y, Chuang SSC (2000) J Catal 190:75
44. Kantcheva M (2001) J Catal 204:479
45. Kantcheva M, Samarskaya O, Ilieva L, Panataleo G, Venezia AM, Andreeva D (2009) Appl Catal B 357:159
46. Sadykov VA, Lunin VV, Matyshak VA, Paukshtis EA, Rozovskii AYa, Bulgakov NN, Ross JRH (2003) Kinet Catal 44:379
47. Radtke F, Koeppel RA, Minardi EG, Baiker A (1997) J Catal 167:127
48. Anderson JA, Marquez-Alvarez C, Lopez-Minoz MJ, Rodriguez-Ramos I, Guerrero-Ruiz A (1997) Appl Catal B 14:189
49. Kumar PA, Reddy MP, Ju LK, Hyun-Sook B, Phil HH (2008) J Mol Catal A 291:66
50. Kameoka S, Chafik T, Ukisu Y, Miyadera T (1998) Catal Lett 51:11
51. Beloshapkin SA, Matyshak VA, Paukshtis EA, Sadykov VA, Ilyichev AN, Ukharskii AA, Lunin VV (1999) React Kinet Catal Lett 66:297
52. Zuzaniuk V, Meunier FC, Ross JRH (2001) J Catal 202:340
53. Yeom YH, Li M, Sachtler WMH, Weitz E (2006) J Catal 238:100
54. Pearson RG, Anderson DH, Alt LL (1955) J Am Chem Soc 77:527